Degradation and structure change of humic acids corresponding to water decline in Zoige peatland, Qinghai-Tibet Plateau

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HIGHLIGHTS

► HAs were decomposed significantly due to water loss in Zoige peatland.
► Water loss induced a significant shift in FT-IR and ^{13}C NMR spectra of HAs.
► The ratio of aliphatic to O-aliphatic carbon (A/O-A ratio) dramatically increased.
► The aromaticity of HAs increased with water loss in the higher-altitude site.

ARTICLE INFO

ABSTRACT

As the largest plateau-type wetland in the world and the largest peat storage in China, Zoige wetland faces severe water decline, and consequently accelerated peat degradation and carbon emission. Here, a variety of characterization approaches, including elemental analysis, UV–vis spectra, FT-IR spectra, and solid state ^{13}C NMR spectra were used to investigate the degradation and the structural shift of humic acids (HAs) in correspondence with serious water loss in Zoige peatland. Water loss derived from both natural slope and artificial drainage caused a substantial degradation of organic matter and HAs. Compared with the blocks immersed by free surface water, HAs extracted from the drier blocks had more pronounced signals of carboxyl and carbonyl groups, but carried lower content of methoxyl, carbohydrate, alcohol and ether groups. The total aliphatic carbon in HAs from natural-slope drier site decreased almost one half, but in the artificial-drained site, only slightly decreased. Correspondingly, the HA aromaticity substantially increased in the site undergoing the longer time of aerobic oxidation, whereas varied little in the site impacted by extensive water leaching.

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1. Introduction

Covering 1.2×10^4 km^2, and located in the northeast of Qinghai-Tibet Plateau with an altitude of over 3400 m above sea level, Zoige wetland is the largest plateau-type wetland in the world (Fei, 2006; Li, 2008; Xiang et al., 2009). It is the major water source of the world largest plateau reserve, Three-river Sources Reserve, supplies water source to three most essential rivers of East Asia, including Huanghe River, Yangzte River and Lancang River (called MeKong River in Southeast Asia). Comprised primarily of peat bogs, Zoige wetland is the largest peat deposition in China (Fei, 2006). Carbon storage of the peat bogs in Zoige is estimated to be 5.54 Pg, accounting for 6.2% of organic carbon storage of China (Gao, 2007). As a combined result of climate change and artificial drainage to enlarge pastures and to tap peat resources, however, the water table in Zoige peat-wetland faces severe decline (Xiang et al., 2009). According to the report, the total area of Zoige wetland has shrunk by more than 30% in the past three decades (Gao, 2006). Induced by the

decline of water table as a result of climate change and artificial drainage, the enhanced decomposition of peat deposit and the accelerated carbon emission from peat respiration become the potential ecosystem crisis in Zoige wetland.

Peatlands in natural state are considered to be sinks of carbon, sequestering large quantities of organic carbon (Clymo, 1984; Gorham, 1991; Alm et al., 1997) via the uptake of large amounts of carbon dioxide from the atmosphere and storing them as peat, even though they emit small quantities of carbon dioxide and methane simultaneously (Moore and Knowles, 1987; Moore and Knowles, 1989). The procedure of peat accumulation in these bogs depends largely on the water table, which controls the production–decomposition mass balance of organic carbon in peat (Clymo, 1983, 1984; Gorham, 1988; Riutta et al., 2007). Water saturation creates an anaerobic marsh environment, slows the decomposition rate of organic carbon deposits, and then enhances the stability of peat effectively (Clymo, 1984; Ingram, 1978; Ise et al., 2008). On the contrary, the decline of water table may stop or even reverse the peat accumulation process, resulting in the conversion of these peatlands into sources of volatile carbon (Armentano and Meges, 1986; Hogg et al., 1992; Updegraff et al., 2001).

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The variation of water content is considered as the driving factor influencing the peatland ecosystem, surpassing the other variations of environmental conditions, i.e. temperature and plant community (Moore, 2002). For example, peat soils saturated with water had no significant change even at high temperature, but when exposed to air (Hogg et al., 1992) or well-drained (Wickland and Neff, 2008), their deterioration was intensively promoted. Some hydrological and ecological models were recently employed to investigate the quantitative relation between water level and peat mineralization (Riutta et al., 2007; Renger et al., 2002). Microbial community analysis indicated that water loss stimulated the growth of both fungal and bacterial biomass in the peatland. The enhanced bio-activities finally yielded a threefold increase of carbon emission (Jaatinen et al., 2008).

As the core complexes of organic matter in peat, HAs play the most important role in the sustainment of peat (Thurman, 1985). Due to their amphipathic nature, HAs may interact with various inorganic and organic substances through chemical bonding or non-specific physical interactions, and greatly affect the cycling and bioavailability of chemical components in peats (Stevenson, 1994; Li et al., 2003). However, the degradation and structure modification of the core component in peat, humic acids (HAs), in correspondence to the water loss derived from the climate change or human activities, so far has received less attention. In this study, using various characterization techniques, we systematically analyzed the structure feature of the HA extractions from the peats of Zoige in different hydrological conditions. The goal of this research was to discover the relationship between the degradation and structure changes of HAs and the severe water loss due to natural drying and artificial drainage in Zoige wetland, the largest plateau-type wetland in the world and the largest peat storage in China. In terms of the structure change of HAs, this study may give an insight into the molecular mechanisms of peat degradation and carbon emission from the water-declined peatland.

2. Methods and materials

2.1. Site description and sampling

The two studied peat bogs are located in Hongyuan, Sichuan Province of China, with an average annual precipitation of 657–753 mm and an average annual temperature of 0.7–1.1 °C. The study sites vary in the cause of water table decline, respectively due to the altitude variation and artificial drainage in the 1970s. The 'slope-controlled (SC)' site with different altitude along the natural slope is located in a core area of Zoige wetland (32°28′19.5″, 102°22′5.4″), with little disturbance from human activities. The 'artificial drainage-controlled (ADC)' site is located in a transitional area (32°26′2.8″, 102°22′41.2″), with a grazing block completely converted into meadow due to artificial drainage. Each site was divided into two blocks according to the gradient of surface water table, which are I block (surface water table at 20–30 cm) and II block (no free surface water), respectively. The experimental setup was randomized complete block design with three replicates for each block. The sample area of each site was about 2–4 ha. Each sample taking into the lab was composted of 5 small-samples, which were randomly collected in the sample site and homogenized. The moist of the peatland differed in different sampling sites with varied depths. The soil moisture of samples from the SC I and ADC I was 60–90%. The samples from the drier site in the top 0–20 cm, such as SC II and ADC II, had the soil moisture of 30–70%. Three topsoil (0–20 cm) samples, collected from each block in August 2008, were air-dried at 30 °C for a week, milled and sieved through a 0.15 mm mesh sieve after the plant roots were manually removed.

2.2. Extraction of HAs

The extraction of HAs was conducted via the procedure recommended by International Humic Substance Society (Swift, 1996). Briefly, one gram sample was mixed with 0.1 M HCl (solid/solution ratio of weight is 1:10) in centrifuge tube. The pH of solution was adjusted to 1–2 with 1.0 M HCl. The mixture was equilibrated by continuous tumbling for 1 h and then centrifuged. After that, the supernatant was decanted, residue was neutralized with 1 M NaOH and thereafter solution of 0.1 M NaOH was added to achieve the solid/solution ratio of 1:10 under nitrogen atmosphere. The suspension was shaking for 4 h and then settled overnight. The solution phase, separated through centrifugation, was collected. The procedure of base extraction above was repeated for 4 times until the color of suspension turned into light-brown to ensure that all HAs were exhausted. In a stirring device, the solution from all these four sub-extractions was acidified to pH 1.0 with 6 M HCl, and allowed to stand overnight. Again after centrifugation and decanting the supernatant, the HAs precipitated was dissolved by potassium hydroxide solution under nitrogen atmosphere. Subsequently 0.3 M of K^+ in solution was reached by addition of KCl salt and the residue of fine mineral particles was removed by centrifugation. Again after the acidification, precipitation and centrifugation in sequence, the HA slurry was treated with a mixed solution of HCl and HF for 16 h, dialyzed against distilled water, freeze-dried and stored for characterization. All the steps performed in the extraction were carried out in room temperature, which was maintained at 25 ± 2 °C.

2.3. Characterization of HAs

Elemental composition was measured by an elemental analyzer (Vario EI III, Elementar, Germany) through a standard high-temperature combustion procedure. The UV–vis spectra of HA extractions were collected by a Cary 50 UV–vis spectrophotometer (Varian, US). The E_4/E_6 ratios (the ratio of the absorbance at 465 nm to that at 665 nm) were calculated according to Chen (Chen et al., 1977). The FT-IR spectra of HA extractions were recorded for a wavenumber range of 4000 to 400 cm^{-1} by a Nicolet 380 FT-IR spectrometer (Thermo, US). Before the FT-IR analysis, the powdered mixtures containing 1 mg HA sample and 60 mg KBr were compressed into pellet. The solid-state ^{13}C NMR spectra were obtained on an Infinity Plus 300 WB spectrometer (Varian, US) operated at 75 MHz, with a magic angle-spinning (MAS) rate of 10 kHz, recycle time of 1.2 s and contact time of 1 ms. Samples (100 mg) were filled in a 4-mm-zirconia rotor with a KEl-F cap. Chemical shifts were externally referenced to the glycine resonance at 176 ppm.

3. Results

3.1. The organic matter, extraction yield and the elemental composition

The extraction yield of HAs and organic matter content from the peat samples is presented in Fig. 1. Table 1 shows the elemental composition, the atomic ratio and E_4/E_6 ratios of HAs from each site. In comparison with the blocks covering surface water (SC I and ADC I), the content of organic matter from the drier blocks (SC II and ADC II) decreased by 40% and 37%, respectively. The extraction results indicated a significant decrease of HAs in the sites confronted with water loss. Specifically, the extraction yields of HAs decreased from 214 and 208 g/kg for the wetter blocks (SC I and ADC I) to 160 and 144 g/kg for the drier blocks (SC II and ADC II), respectively. The percentage of HAs loss was 25% for SC II, and 31% for ADC II, indicating a less decomposition rate of HAs in comparison with the total organic matter. There was no distinguished difference of C content in the HAs between SC I and SC II, also between ADC I and ADC II. The N content of HAs from the wetter blocks (SC I and ADC I) was relatively higher than those in the drier blocks (SC II and ADC II). Consequently, with reduction of water in the drier blocks, the HA atomic C/N ratio tended to increase. The value of E_4/E_6 ratio and H/C for the SC II drier block was lower than those from SC I moister block.